1 479 913

# PATENT SPECIFICATION

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(19)


## (54) PROCESS FOR SURFACE-SIZING PAPER

(71) We, BASF AKTIENGESELLSCHAFT, a German Joint Stock Company of 6700 Ludwigshafen, Federal Republic of Germany, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following Statement:—

This invention relates to a process for the manufacture of surface-sized paper by impregnating paper with an aqueous solution containing 0.1 to 5% by weight of a random copolymer in salt form obtained by copolymerization of

(a) from 50 to 90% by weight of one or more $\alpha$-olefins of from 2 to 12 carbon atoms,

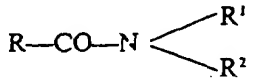
(b) from 50 to 10% by weight of acrylic acid and/or methacrylic acid and, optionally,

(c) up to 30% by weight of one or more non-basic polymerizable compounds, and neutralization of the polymeric product to give a copolymer having a K value of from 20 to 40, and drying the impregnated paper. Such a process is hereinafter referred to as a process of the type defined.

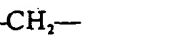
It is well known to engine-size paper using rosin and related substances (sizes) and aluminum(III) or iron(III) salts. German Published Application 2,040,692 discloses a method of sizing paper with the aid of water-soluble salts of random copolymers of an olefin of from 2 to 12 carbon atoms and acrylic and/or methacrylic acid and optionally containing up to 30% of other non-basic polymerizable compounds. However, the degree of sizing of the papers thus produced and the processability of the aqueous solution of salts of the random copolymer are unsatisfactory.

The present invention seeks to improve a process of the type defined so as to produce better sizing and improved processability of the polymer solutions.

According to the present invention there is provided a process of the type defined wherein the aqueous solution for impregnation of the paper additionally contains from 0.1 to 20% by weight of a compound of the general formula:

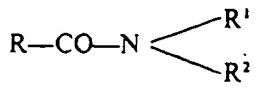


in which R denotes hydrogen, alkyl, aryl or $NR^1R^2$, $R^1$ and $R^2$ together denote alkylene or each independently denote hydrogen, alkyl, aryl or a radical of the formula



and $R^3$ denotes hydrogen, alkyl or aryl.

The invention also provides a composition for the surface sizing of paper comprising a random copolymer as defined above in salt form and a compound of the formula



as specified above.

The $\alpha$-olefin or olefins (a) forming one component of the copolymers preferably contain from 2 to 8 carbon atoms. A particularly suitable $\alpha$-olefin is styrene. The proportion of this component is preferably from 60 to 85% by weight. The preferred comonomer (b) is acrylic acid and examples of comonomers (c) which are optionally present are acrylonitrile, methacrylonitrile, acrylamide, methacrylamide, $C_{1-4}$ alkyl esters of acrylic acid and methacrylic acid and vinyl esters of $C_{2-4}$ alkanoic acids and vinyl chloride.

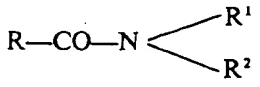
The copolymers may be prepared in known manner by suspension or solution polymerization in an aliphatic, cycloaliphatic or aromatic hydrocarbon including, for example, an $\alpha$-olefin such as ethylene, propene, isobutene or in an alcohol such as ethylene glycol, isopropanol and isobutanol, at a temperature from 60° to 130°C in the presence of a free-radical initiator such as an azo compound, peroxide or hydroperoxide, e.g. azobisisobutyronitrile and lauroyl peroxide. A chain stopper may also be present during polymerization, for example carbon tetrachloride, cyclohexane or lauroyl mercaptan. Preferably, the copolymer is prepared by solution polymerization in a primary or secondary $C_{1-4}$ alcohol or alcohol mixture at from 60 to 130°C, more preferably from 80° to 120°C. The initiator is preferably used in an amount of from 0.01 to 1% by weight of the comonomers and the chain stopper in an amount of from 0.001 to 0.5% by weight.

In order to prepare a highly random copolymer, it is recommended that the monomer (b) is first placed in the vessel and the remaining monomer or monomers are added in the course of polymerization. The solids content of the dispersion is from 10 to 50%, preferably from 25 to 35%, by weight.

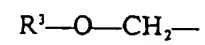
In order to render the copolymer, which contains free carboxyl groups or anhydride groups, water-soluble, it is neutralized, i.e. converted to a salt with a base, although it is not necessary to neutralize all of the carboxyl groups, since generally a degree of neutralization of 80%, based on the total number of carboxyl groups, is sufficient. The concentration of the salt of the random copolymer in the solution is from 0.1 to 5%, preferably from 0.4 to 3%, by weight.

Particularly suitable cations are ammonium or mono-, di- or tri-alkylammonium having a total of up to 6 carbon atoms and also for example sodium and/or potassium. These cations may be introduced into the copolymers by converting them with, inter alia, ammonia and the free organic amines or caustic alkalis. To bind the free ammonia or amines it has been found advantageous to add formaldehyde or other aliphatic aldehydes such as glyoxal, which may be used in amounts of from 0.5 to 25%, based on the weight of copolymer.

According to the invention, the aqueous solution of a water-soluble random copolymer of an olefin and acrylic and/or methacrylic acid used for surface-sizing of paper is blended with from 0.1 to 20% by weight, based on the solution, of a compound of the general formula:

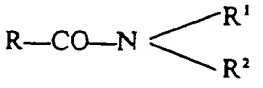


in which R denotes hydrogen, alkyl, aryl or $NR^1R^2$, $R^1$ and $R^2$ together denote alkylene or each independently denote hydrogen, alkyl, aryl or a radical of the formula:



and $R^3$ denotes hydrogen, alkyl or aryl.

Suitable compounds of the general formula:



are for example formamide, dimethyl formamide, acetamide, dimethyl acetamide, urea and substituted ureas. We prefer to use urea, dimethyl acetamide and

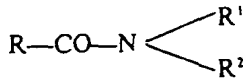
substituted ureas such as N,N-dimethyl urea, ethylene urea, propylene urea, dimethoxymethylol urea and dimethylol urea.

The substituent R may apart from hydrogen be for example alkyl of from 1 to 12 carbon atoms, aryl, optionally substituted, or an $NH_2$ group in which one or both of the hydrogen atoms may be replaced by alkyl, aryl, hydroxymethyl, alkoxymethyl or aryloxymethyl substituents. By the term "alkyl groups" we include cycloalkyl groups, particularly those in which the carbon ring contains from 3 to 12 carbon atoms. The cycloalkyl groups may also carry substituents.

The amount of copolymer required for paper sizing is generally from 0.05 to 5% by weight and preferably from 0.1 to 1.5% by weight, based on the weight of the fibrous substance. If aluminum(III) or iron(III) salts such as aluminum sulfate or iron sulfate are included in the size, the preferred ratio of copolymer to these cations is from 1:10 to 1:300, by weight.

For white papers it is recommended to use aluminum salts, whilst iron(III) salts can be used where a brownish yellow tinge is acceptable, in both cases the amount used generally being from 0.005 to 0.5% of cation and preferably from 0.02 to 0.1% of cation, by weight of the fibrous substance. It is advantageous to add the salts to the pulp but it is also possible to impregnate the finished paper with a solution of the salts prior to treatment with the copolymer.

In addition to the solution of a salt of a copolymer and a compound of the general formula:



used in the process of the invention for surface-sizing paper, it is possible to include other non-ionic or anionic sizing agents such as rosin size. Generally speaking, the agents which characterize the invention show good compatibility with paper auxiliaries such as fillers, pigments, dyes, wet-strengtheners, brighteners and other agents. This applies to the manufacture of sized papers of all thicknesses and types including, for example, papers and cardboards of bleached and unbleached sulfite cellulose or sulfate cellulose and groundwood.

The method of sizing employed when using the agents which characterize the invention may in general be the same as the conventional methods of surface-sizing and, consequently, no further details are required in this specification. A web of paper is impregnated and then dried. The additives proposed according to the invention are ineffective when added to the suspension of fibers prior to sheet information.

In accordance with the invention, there are obtained very well sized papers. The solutions used for this surface-sizing exhibit good filler-compatibility and improved processability over solutions not containing the additives of the invention: for example, it is easier to form a homogeneous mixture with water.

In the following Examples the percentages are by weight unless otherwise stated. The K values of the copolymers were determined by the method proposed by H. Fikentscher in Cellulosechemie *13*, pp. 58—64 and 71—74 (1932) on 0.5% dimethyl formamide solutions at 20°C. K denotes k x $10^3$.

## EXAMPLE 1.

An approximately 0.5% fiber suspension of 100% bleached sulfite cellulose is processed to a paper weighing 80 g/m² in the usual manner. This paper is then impregnated with an aqueous solution, which contains 2.4% of the ammonium salt (90% salt) of a random solution copolymer of 80% of styrene and 20% of acrylic acid and having a K value of 32 and 10% of urea, based on the weight of the total solution, the dry pickup being 1.2% based on the weight of the paper, which is then dried.

For the purpose of comparison, the same paper was engine-sized in conventional manner with the same weight of rosin size, since this method gives the closest sizing effect.

The degree of sizing was then determined by the Cobb test (DIN mold 53/21—1 min.) and by the ink flotation test (test ink as laid down by DIN 53,126).

The results were as follows:

| Paper | Cobb test after 1 min. | Ink flotation test |
|---|---|---|
| unsized | 140 | strike-through in 0.5 min. |
| conventionally sized (engine-sized) | 50 | ,, ,, 3.0 min. |
| invention | 18 | ,, ,, 4.0 min. |
| invention plus 0.5% of aluminum sulfate, based on fiber | 16 | ,, ,, 5.5 min. |

EXAMPLE 2.

A fiber suspension (38°SR) of 30% of groundwood and 70% of bleached cellulose and containing 14% of kaolin, based on the weight of fiber substance, is processed to paper in the usual manner and treated with the sizing agents described in Example 1.

The quality of the results obtained is demonstrated in the following Table:

| Paper | Cobb test 1 min. | Cobb test 5 min. | Ink flotation test |
|---|---|---|---|
| unsized | 120 | 130 | strike-through in 1 min. |
| conventionally sized (engine-sized) | 15 | 60 | ,, ,, 6 min. |
| invention | 15 | 21 | ,, ,, 12 min. |
| invention plus 1% of aluminum sulfate, based on fiber | 14 | 23 | ,, ,, 13 min. |

EXAMPLE 3.

A fiber suspension of 100% bleached sulfite cellulose containing 12% of kaolin is processed in conventional manner to paper weighing 80 g/m² and is then impregnated with an aqueous solution containing 1.5% of the ammonium salt (100% salt) of a copolymer of 85% of ethylene and 15% of acrylic acid and having a K value of 20, 10% of dimethyl acetamide and 2% of oxidatively degraded starch thus rendered soluble in hot water, the dry pickup being about 1.5%.

For the purpose of comparison, an engine-sized paper is produced in known manner, in which the above copolymer is replaced by an equal weight of rosin size.

The results obtained in tests on the sizing effect are given in the following Table:

| Paper | Cobb test after 1 min. | Ink flotation test |
|---|---|---|
| unsized | 110 | strike-through in 2 min. |
| conventionally sized (engine-sized) | 60 | ,, ,, 4 min. |
| invention | 17 | ,, ,, 5 min. |
| invention plus 3% of aluminum sulfate, based on fiber | 15 | ,, ,, 10 min. |

EXAMPLE 4.

A fiber suspension of bleached sulfite cellulose (100%) containing 12% of kaolin and 1% of a commercially available anionic urea/formaldehyde resin wet-strengthener was processed in conventional manner to a paper weighing 80 g/m². The paper is then impregnated with an aqueous solution containing 2.5% of the methylammonium salt (80% salt) of a copolymer of 85% of styrene and 15% of methacrylic acid and having a K value of 25 and 15% of N,N-dimethyl urea, based on the weight of the solution. The dry pickup is 1.8% and in a parallel test it is 0.9%.

For the purpose of comparison, the same paper was engine-sized in conventional manner using an equal weight of resin size together with the same wet-strengthener. The results of the Cobb test were as follows:

| Paper | Cobb test 5 min. |
|---|---|
| unsized | 112 |
| engine-sized in conventional manner | 45 |
| invention, dry pickup 0.9% | 17 |
| invention, dry pickup 1.8% | 15 |
| invention plus 3% of aluminum sulfate | 10 |

EXAMPLE 5.

A fiber suspension of bleached sulfite cellulose (100%) is processed in conventional manner to a paper weighing 80 g/m² and individual tests are carried out in which this paper is surface-sized (dry pickup 0.8%) with different aqueous solutions containing 0.5% of the ammonium salt (90% salt) of a copolymer of 50% of $\alpha$-olefin and 50% of acrylic acid as listed in the following Table and also containing 5.0%, based on the solution, of ethylene urea. The data obtained in the ink flotation test and Cobb test are listed below:

| $\alpha$-olefin | K value of copolymer | ink resistance | Cobb test 5 min. |
|---|---|---|---|
| $H_2C=CH_2$ | 33 | very good | 24 |
| $H_2C=CH-CH_3$ | 34 | ,, | 20 |
| $H_2C=C(CH_3)_2$ | 29 | ,, | 18 |

EXAMPLE 6.

A fiber suspension of bleached sulfite cellulose (100%) containing 0.5% of sodium aluminate is processed in conventional manner to a paper weighing 80 g/m², which is then surface-sized (dry pickup 1.0%) with an aqueous solution containing 0.5% of the ammonium salt (90% salt) of a copolymer of 80% of styrene and 20% of acrylic acid and having a K value of 36 and 5%, based on the weight of the total solution, of propylene urea. In the ink flotation test, the resulting sized paper gave a value of 11 min (for strike-through).

EXAMPLE 7.

A fiber suspension of bleached sulfite cellulose (100%) is processed in conventional manner to a paper weighing 80 g/m² which is then surface-sized (dry pickup 1.4%) with an aqueous solution containing 0.5% of the ammonium salt (85% salt) of a copolymer of 85% of styrene and 15% of acrylic acid and having a K value of 20 and 10% of $CH_3O-CH_2-NH-CO-NH-CH_2-OCH_3$ (dimethoxymethylol urea). The results were excellent, the value obtained in the Cobb test (5 min.) being about 18.

EXAMPLE 8.

A fiber suspension of 30% of groundwood and 70% of bleached cellulose and

containing 15% of kaolin and 3% of aluminum sulfate is processed in the usual manner to a paper weighing 80 g/m². This paper is then surface-sized (dry pickup 1.2%) with an aqueous solution containing 2% of starch rendered soluble in hot water, 0.5% of the ammonium salt (90% salt) of a copolymer of 80% of styrene, 15% of acrylic acid and 5% of acrylonitrile and having a K value of 32 and 10% of dimethylol urea. The ink flotation time of the resulting sized paper was about 16 minutes and the Cobb test gave values of 16 (1 min.) and 21 (5 min.).

EXAMPLE 9.

A fiber suspension of bleached sulfite cellulose (100%) containing 2% of iron(III) chloride is processed in the usual manner to a paper weighing 80 g/m², which is then surface-sized (dry pickup 0.8%) with an aqueous solution containing 2% of the ammonium salt (95% salt) of a copolymer of 80% of styrene, 15% of methacrylic acid and 5% of methacrylonitrile and having a K value of 32 and 5% of dimethyl acetamide. The yellowish-brown sized paper thus obtained showed good ink resistance.

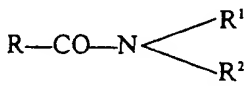
WHAT WE CLAIM IS:—

1. A process for the manufacture of surface-sized paper by impregnating paper with an aqueous solution containing 0.1 to 5% by weight of a random copolymer in salt form obtained by copolymerisation of

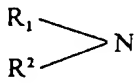
(a) from 50 to 90% by weight of one or more $\alpha$-olefins of from 2 to 12 carbon atoms and

(b) from 50 to 10% by weight of acrylic acid, methacrylic acid or a mixture thereof

and neutralization of the polymeric product to give a copolymer having a K value of from 20 to 40, and drying the impregnated paper, wherein the aqueous solution for impregnation of the paper additionally contains from 0.1 to 20% by weight of a compound of the formula:



where R is hydrogen, alkyl, aryl or a radical of the formula



$R^1$ and $R^2$ together are alkylene or each independently are hydrogen, alkyl, aryl or a radical of the formula:

$$R^3—O—CH_2—$$

and $R^3$ is hydrogen, alkyl or aryl.

2. A process as claimed in claim 1 wherein the random copolymer is obtained by copolymerization of (a), (b) and, as additional comonomer, (c) up to 30% by weight of one or more non-basic polymerizable compounds.

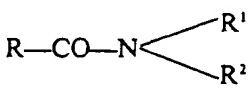
3. A process as claimed in claim 2, wherein component (c) is selected from acrylonitrile, methacrylonitrile, acrylamide, methacrylamide, $C_{1-4}$ alkyl esters of acrylic and methacrylic acids, vinyl esters of $C_{2-4}$ alkanoic acids and vinyl chloride.

4. A process as claimed in any of claims 1 to 3 wherein component (a) of the random copolymer is styrene and component (b) is acrylic acid.

5. A process as claimed in any of claims 1 to 4, wherein the random copolymer is obtained by solution polymerization in a primary or secondary $C_{1-4}$ alcohol or alcohol mixture at from 60° to 130°C.

6. A process as claimed in any of claims 1 to 5, wherein the aqueous solution contains from 0.4 to 3% by weight of the random copolymer in salt form.

7. A process as claimed in any of claims 1 to 6, wherein the compound of the formula:



is urea, dimethyl acetamide, N,N-dimethyl urea, ethylene urea, propylene urea, dimethoxymethylol urea or dimethylol urea.

8. A process as claimed in any of claims 1 to 7, wherein the paper is additionally impregnated with one or more aluminum(III) salts and/or iron(III) salts.

9. A process for the manufacture of surface-sized paper as claimed in claim 1 and carried out substantially as described in any of the foregoing Examples.

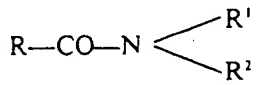
10. Paper which has been surface-sized by a process as claimed in any of claims 1 to 9.

11. A composition for the surface sizing of paper comprising a random copolymer in salt form obtained by copolymerization of

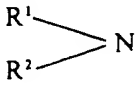
(a) from 50 to 90% by weight of one or more $\alpha$-olefins of from 2 to 12 carbon atoms and

(b) from 50 to 10% by weight of acrylic acid, methacrylic acid or a mixture thereof

and neutralization of the polymeric product to give a copolymer having a K value of from 20 to 40, and a compound of the formula:



where R is hydrogen, alkyl, aryl or a radical of the formula:



$R^1$ and $R^2$ together are alkylene or each independently are hydrogen, alkyl, aryl or a radical of the formula:

$$R^3—O—CH_2—$$

and $R^3$ is hydrogen, alkyl or aryl.

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